UNPUBLISHED PRELIMINARY DATA

Technical Status Report No. 5

CHEMISTRY OF THE ATMOSPHERE OF THE PLANET VENUS

Rensselaer Polytechnic Institute
Troy, New York

1 August 1964 - 31 January 1965

Research Grant No. NSG-261-62
R.P.I. Project 441.68

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Microwave Emission from Chemical Reactions

The measurements of microwave radiation intensities emitted from glow discharges and chemiluminescent reactions were repeated incorporating a Watkins - Johnson traveling wave tube amplifier, Model W J - 276, to provide increased sensitivity. This amplifier was made available for these tests through the cooperation of Mr. H. S. Webb of Ossman Instruments. The use of this amplifier increased the sensitivity of the detection system to about 5×10^{-15} watts. Previously the sensitivity had been 10^{-13} watts. In agreement with previously reported results, emission was readily observed from the glow discharges but no reliable signals could be detected from the atom-molecule reactions. At times weak, unreliable signals near the lower limit of detection seemed to be present, but additional work with more sensitive equipment would be required to determine their validity.

As previously reported, the microwave intensity observed from a glow discharge through SO_2 was between 1.5×10^{-9} and 2.5×10^{-8} watts, or about six orders of magnitude over the limit of detection. The visible light intensity from the atom molecule reaction,

$$SO + O \rightarrow SO_2 + h\nu \qquad (1)$$

generated by addition of O-atoms to COS, was substantially less than that from the glow discharge, but almost certainly not as much as six orders of magnitude less. Allowing for losses of 2-3 orders of mag-

nitude in the waveguide systems used detection of signals from atom-molecule reactions, the difference is reduced to 3-4 orders of magnitude and the intensity ratio between the two types of visible light emission may be in the range. It is thus difficult to say positively whether the observed microwave emission originates predominantly from the simple chemiluminescent reaction or from some more complicated ion reaction occuring in the discharge. This is even more true in the case of CO_2 where the observed microwave intensity from the glow discharge is only 2×10^{-11} watts.

For both these gases, however, the observed intensities are orders of magnitude higher than can be accounted for by thermal effects including electron temperature. Such origins must thus be taken into account in deriving a temperature for Venus from microwave data. Experiments in this area are continuing.

An Alternate method for determining whether microwave radiation is emitted from reactions such as NO + O, or SO + O would be to observe with a radiotelescope the luminescence from a rocket release of NO, COS, or CO in the earth's atmosphere. The limits of sensitivity would be much lower and the results could be definitive.

Photochemistry with Bromine Lamp

Experiments have been carried out using the bromine lamp which emits the persistent bromine line at 1633 A. The first lamp was constructed like a condenser with the inner tube made of Suprasil quartz for transmission of the bromine line. Bromine vapor was admitted through a capillary leak and argon was used as a carrier gas just as was done with the iodine lamp. Gases to be irradiated were contained in the

jacket. Since this lamp operated satisfactorily, a more complex lamp was constructed which permitted gas samples to be irradiated at various temperatures. The new lamp had a water-cooled finger lengthwise through the discharge tube and an insulating vacuum jacket between the discharge tube and the sample jacket. An additional outer jacket was provided through which water or other coolant could be circulated so the irradiations could be carried out at any desired temperature.

The equilibrium between oxygen and ozone was studied initially by flowing oxygen or oxygen-ozone mixtures through the sample jacket. The ozone content of the irradiated gas was determined by bubbling through potassium iodide solution and titrating the liberated iodine with standard sodium thiosulfate. The first results gave an equilibrium ozone concentration of only about 1% and showed that ozone was destroyed about ten times as fast as it was formed. However, by flowing oxygen through the vacuum jacket to filter out the 1633 A line while transmitting wavelengths above ~ 2000 A, it was found that ozone was being destroyed by the bromine continua between 2500 and 3000 A. Although these were relatively weak, integrated over the entire wavelength region their intensity was about 10^{18} quanta/sec compared to about 10^{17} for the 1633 A line. By using a smaller leak and by cooling the bromine with ice and salt this ratio was reduced so that the intensities were about 5×10^{15} for the continua and about 3×10^{16} for the 1633 A line. Under these conditions a series of irradiations has been carried out on pure oxygen at several pressures at 273^{0} K and 201^{0} K, irradiating in each case for several hours until equilibrium had been reached. If it is assumed that ozone formation and destruction proceed according to the following well-

known mechanism:

$$O_2 + h\nu \rightarrow O + O \qquad (1)$$

$$O_2 + O + M \rightarrow O_3 + M \qquad (2)$$

$$O_3 + O \rightarrow 2O_2 \qquad (3)$$

then in pure oxygen the equilibrium ozone pressure should vary with the square of the oxygen pressure:

$$[O_3] = \frac{k_2}{k_3} [O_2] [M]$$

or in pure oxygen

$$[O_3] = \frac{k_2}{k_3} [O_2]^2$$

Instead it was found that the ozone pressure varied linearly with oxygen pressure at both temperatures. At 201°K the equilibrium O_3/O_2 ratio was ~ 0.4. and at 273°K the ratio was ~ 0.1. These results show that the above mechanism is not dominant under these conitions as had been thought. An alternate mechanism involving excited molecules and atoms, perhaps with excess kinetic energy, is under consideration. Because the high intensity of this lamp permits equilibrium data to be obtained fairly easily, it may be possible to understand some of the discrepancies between different values reported in the literature.

Preliminary experiments have also been made on CO_2 at 201°k and 150mm. The irradiation was not carried to equilibrium but about 9% of the CO_2 was dissociated. Ozone was present and the ratio of O_3 to O_2 was about 0.4 in agreement with that found for pure O_2 at this temperature. These experiments with CO_2 are particularly pertinent to the Venus atmosphere and will be extended, but a knowledge of the O_2-O_3 system is a prerequisite to an understanding of the O_2-O_3-CO-CO_2 system under pseudo-solar radiation conditions.

Photochemistry with Iodine Lamp

In related work a series of experiments studying the effect of the 2062 A radiation on a variety of organic compounds is now in progress. Dr. Galli, a NATO Fellow from Italy is conducting these experiments.

CO + O + M Reaction

A relatively small, but important study is being carried out on the reaction of carbon monoxide with oxygen atoms. This work is being aided by a graduate student, A. Bergendahl, who will use the results to fulfill his requirements for the Master's degree.

All reactions in the CO - CO_2 - oxygen atom system are of fundamental importance for the chemistry of the Venus atmosphere since CO_2 is a major constituent. The results of studies on the CO - O-atom reaction in the literature to date are not very reliable for a variety of reasons. By using the mass spectrometer (purchased under a previous NASA grant) which is attached to a low pressure reaction system, it is believed that more accurate results can be obtained than those already reported.

Although the work on this CO-oxygen atom reaction has been in progress only a few months, earlier preparation had been made including studies of techniques and equipment modification necessary. Therefore the work is expected to be submitted to a journal for publication within the next few months, probably by the end of June.

Presentations

A paper entitled " The Bromine Lamp: A New Source of Ultraviolet Radiation" is scheduled for presentation at the American Chemical Society Meeting in Detroit, April 5-9, 1965.